

967,934



PATENT SPECIFICATION

NO DRAWINGS

967,934

Date of Application and filing Complete Specification Feb. 6, 1961.

No. 4422/61.

Application made in France (No. 841,651) on Oct. 20, 1960.

Complete Specification Published Aug. 26, 1964.

© Crown Copyright 1964.

Index at acceptance: —C1 A(H11I, H12B, H12X, H13, H14A, H14H); C1 J(4, 5, 9, 14, 19, 23, 35); C4 A9A

International Classification: —B 01 f (C 04 b, C 09 d)

COMPLETE SPECIFICATION

Silica Sols and Refractory Materials Prepared Therewith

I, AUGUSTE LESCHOT, a French citizen, of 77, boulevard Paul Vaillant-Couturier, Montrouev (Seine) France, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of a silica organosol, which can be used more particularly as binder for highly refractory materials, and which comprises substantially a silica sol in a mainly organic medium, having a low water content and a negligible content of inorganic salts.

It is known that in the manufacture of refractory elements it is current usage to employ mixtures of suitably ground refractory materials, such as silica, alumina, magnesia, zirconia and various carbides and silicates, with a binder, consisting either of slightly moist colloidal clay or of a silica sol in an aqueous or organic medium, to which may be added small quantities of various substances and especially calcined magnesia, which acts as accelerator in the formation of silica gel.

The water or organic solvent is then removed from the body of the element by means of an evaporation, the rate of which must be controlled so as not to spoil the element, and in this connection it should be noted that the removal of an organic solvent is generally much easier to carry out, owing to its higher volatility or to the possibility of burning it off in the open air.

On these lines, it has been proposed to use ethyl silicate, which by hydrolysis produces silica gel and ethyl alcohol, which is easy to remove. The high cost of ethyl silicate, however, restricts its industrial application.

It has also been proposed to prepare an organosol of silica by starting with a hydrosol

obtained by the action of an acid, such as hydrochloric acid, on a water-soluble inorganic silicate. The hydrosol thus obtained is first of all subjected to a salting-out operation for reducing the water content, consisting in the addition of a salt of the acid used for attacking the inorganic silicate, and of an organic dispersion medium for silica, such as acetone. In these conditions, it is seen that two layers are formed, the lower aqueous layer containing almost all the salt and the upper layer consisting of an organo-hydrosol of silica. The upper layer, separated by decantation, is subsequently subjected to an operation of osmosis through a semi-permeable membrane, such as parchment, with the object of replacing by an organic solvent the water left in the mixture.

The silica sol produced by such a process contains a not negligible percentage of salt corresponding to the acid used in the preparation of the salt, for example sodium chloride or sulphate, and the presence of this salt has the effect of lowering the melting point of the silica, which is a serious drawback in the binding of highly refractory materials.

The present invention makes it possible to avoid this drawback and provides a process for the preparation of a silica sol composed of colloidal silica, organic solvents, and water, comprising the successive steps of forming in known manner a silica organohydrosol composed of colloidal silica, one or more organic solvents, water and inorganic salts, adding to this organohydrosol an oxygen-containing solvent miscible or partially miscible with water, for example acetone, dioxan, methyl alcohol, ethyl alcohol, normal propyl alcohol, isopropyl alcohol, tertiary butyl alcohol, or a mixture of such solvents, in sufficient quantity to produce the precipitation or flocculation of the inorganic salts

45

50

55

60

65

70

75

80

85

it contains, and removing the precipitated or flocculated inorganic salts.

The application of the process according to the present invention makes it possible to

5 prepare under economical conditions a silica sol in an organic or quasi-organic medium, the preferred sols having the following composition by weight:

10	Silica	- - - - -	- - : from 8% to 35%
	Water	- - - - -	- - : less than 5%
	Inorganic salts	- - - - -	- - : less than 0.1%
	Oxygen-containing Organic solvent	: from 60% to 92%	

15 The process of preparing the silica sol hereinbefore defined normally comprises first of all the action of an inorganic acid on an alkaline silicate in aqueous solution, then the conversion of the hydrosol to an organo-

20 hydrosol by osmosis and/or salting out, employing any known means. Typically, an organo-hydrosol having the following composition by weight is thus obtained:

25	Silica	- - - - -	- - : from 15% to 30%
	Water	- - - - -	- - : from 15% to 20%
	Inorganic salts	- - - - -	- - : from 2% to 3%
	Oxygen-containing Organic solvent	: from 47% to 68%	

30 An important feature of the process according to the present invention consists in the precipitation or flocculation of the inorganic salts contained in the above-mentioned organo-hydrosol by means of an addition of tertiary butyl alcohol or other oxygen-containing organic solvent or solvents miscible with water, such as those previously mentioned, the proportion of added solvent being 70 variable according to the nature of the said solvent, and being, for example, about 50% in the case of acetone or dioxan. Once the inorganic salts have been precipitated or 75 flocculated, they are removed, for example by filtration, centrifuging or decantation. It should be noted that the above-mentioned purification stage can be carried out entirely at the ordinary temperature, which forms an appreciable advantage of convenience in 80 carrying out the process.

40 The foregoing purification operation entails some reduction in the silica content of the organo-hydrosol, and in certain cases this content may become less than 10%, 85 which is too low for various applications.

45 The concentration of the previously obtained silica sol may be increased or adjusted by the addition of a suitable quantity of silicon tetrachloride, SiCl_4 , this addition 90 being effected with vigorous stirring of the mixture, and the hydrochloric acid formed being removed by blowing dry air through the sol or by means of an anion-exchange resin, such as a polyamide resin, in the hydroxyl form. A supplementary advantage resulting from the addition of SiCl_4 is the effective 95 dehydration of the silica sol.

55 The silica concentration may be conveniently increased, and at the same time the water content of the silica sol reduced, by the addition of a suitable quantity of ethyl silicate, for example ethyl silicate with 100 40% silica, which can be obtained com-

mercially in a perfectly stable purified form.

55 Another embodiment of the process comprises the concentration of the silica sol produced in accordance with the invention by means of an addition of an organic solvent miscible with the solvent (or solvents) contained in the silica sol and which is not a dispersion medium for silica under the conditions employed, more particularly by means of an addition of spirit of turpentine, trichlorethylene, diisobutylene, benzene or a mixture of these solvents.

60 The quantity of solvent thus added is preferably between 25 and 40% by volume of the sol treated. In these conditions the formation of two layers is observed, one containing the whole of the silica and the other consisting of a mixture of the initial solvent and the added solvent.

65 Although by proceeding in this way the concentration of silica in the sol may be easily increased above 30%, adjustments of concentration may be likewise effected, as indicated hereinbefore, by the addition of SiCl_4 or ethyl silicate, such additions furthermore possessing a dehydrating character which may be of interest in certain applications. In the case of SiCl_4 , the hydrochloric acid is removed as previously described.

70 It should here be remarked that the different operations forming the process according to the invention, and more particularly those relating to the purification of the silica sol, have favourable consequences as regards improving the stability of the silica sol.

75 It has thus been found that, after precipitation of the salts and after filtration, the period of stability of the sol attained the following durations, depending on the nature of the added solvent, if sols having a silica concentration equal to 15% are prepared in 110 the different cases:

- 1 day with tertiary butyl alcohol,
 —3 days with isopropyl alcohol,
 —6 days with ethyl alcohol,
 —7 days with methyl alcohol,
 5 —3 weeks with diexan,
 —4 weeks with acetone.

It has been found possible to obtain an increase in stability of the silica sol by the addition of small quantities (for example 0.5—
 10 10 mole percent on the quantity of silica) of aluminium ions in the form of inorganic salts, such as aluminium chloride, or in the form of organic salts, such as aluminium isopropylate or acetate.
 15 To provide a more exact idea of the present invention, several embodiments of the invention will now be described, by way of non-restrictive example, in which in order not to burden the description it will be assumed that
 20 a start is made with silica organo-hydrosols prepared according to the process described in Industrial and Engineering Chemistry, 39, 1379 (1947) by Iler and Pinkney. According to this process as set out at page 1380, a
 25 dilute solute of sodium silicate—in the present case having preferably a concentration of 1.3N and a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.9—is passed slowly in a thin stream into a violently agitated solution of dilute acid—for example 6N sulphuric acid—maintained at temperature below 30° C—preferably at 0° C. An organic solvent containing polar groups—in the present case preferably isopropyl alcohol—is then added and the mixture allowed to stand. Thereafter sodium chloride is stirred in to saturate the aqueous phase and after this has been allowed to stand the saline layer is drawn off to leave the desired silica organo-hydrosol. The concentration of the
 40 silica sol can be varied by varying the quantity of the solvent which is added.

A—PREPARATION OF A PURIFIED SILICA ORGANOSOL:

- EXAMPLE 1.—A silica organo-hydrosol is used
 45 having the following composition by weight: silica 23%, sodium chloride 2.5%, organic solvent 74.5%. The organic solvent consists of an aqueous solution of isopropyl alcohol containing about 85% alcohol.
 50 To 400 grams of this silica organo-hydrosol is added 215 grams of 1:4-dioxan, and the precipitation of the whole of the sodium chloride is observed. Filtration is then carried out.
 55 EXAMPLE 2.—To 400 grams of the organo-hydrosol, as described in Example 1, is added 180 cc acetone, which results in the precipitation and flocculation of the whole of the sodium chloride. The precipitated salt is
 60 then removed by filtration.

B—PREPARATION OF PURIFIED AND CONCENTRATED SILICA ORGANOSOL.

EXAMPLE 3.—To 250 grams of silica sol purified as indicated in Example 1, there is gradually added with vigorous agitation 27 grams of silicon tetrachloride. Dehydration of the medium and an increase in the concentration of colloidal silica occur simultaneously. The hydrochloric acid formed is removed by blowing dry air through the solution. The same process can be applied to a sol purified by the method of Example 2. Moreover, the hydrochloric acid can be removed by means of an ion-exchange resin of the polyamide resin type.

EXAMPLE 4.—500 grams of an ethyl silicate containing 40% of SiO_2 is added to 1200 grams of an organosol purified by treatment as in Example 1 and containing 12% of SiO_2 . After mixing, there is obtained an entirely anhydrous sol containing 20% SiO_2 , the stability of which has been distinctly improved. The same procedure can be applied to the product of Example 2.

EXAMPLE 5.—1500 grams of silica sol purified according to Example 1 is taken, and 300 grams of benzene is added thereto. After agitation the mixture is allowed to stand, and the formation of two layers is observed. The upper layer of about 620 grams, consisting essentially of a mixture of benzene and isopropyl alcohol, is removed, and the lower alcoholic layer, containing all the silica, the concentration of which attains 31%, is collected.

EXAMPLE 6.—30 grams of a silica sol, purified by a treatment as described in Example 1 and containing 17% of silica, is taken. 10 cc of diisobutylene is added and the mixture is agitated. After standing two layers are formed, and the whole of the silica collects in the lower layer, where the silica concentration attains 30%.

EXAMPLE 7.—100 grams of a silica sol, purified by a treatment as described in Example 1 and containing 16% silica, is taken. 40 cc of spirit of turpentine is added and the mixture is agitated. After standing two layers are formed, and the whole of the silica collects in the lower layer, in which the silica concentration is about 30%.

EXAMPLE 8.—100 grams of a silica sol, purified by a treatment as described in Example 1 and containing 16% of silica, is taken. 25cc of trichlorethylene is added. After agitation and standing the mixture separates into two layers, the upper layer of 34 cc containing the whole of the silica.

- In the Examples 5, 6, 7 and 8 in which a concentration of the silica sol is effected by means of a third solvent, and in which there is finally separated a layer containing the said third solvent mixed with a part of the initial organic solvent, it is quite evident that it will be possible to subject the said layer to distillation or other form of fractionation with a view to the re-utilisation of the components.
- Among the various applications to which the present invention may give rise, may be mentioned in the first place the binding or agglomeration of powdered materials for the purpose of producing highly refractory elements, which can be used in the construction of furnaces or as catalysts. Depending on the technique employed there may be obtained bodies of various densities including both very dense and very porous bodies. The latter case is desirable more particularly in the production of catalysts having a very large active surface. The fine, powdered material is then mixed with the purified silica sol, and there is added a setting accelerator, which may be calcined magnesia, giving hardening in less than a minute by the formation of silica gel. By way of example, if it is necessary to bind alumina in order to obtain small moulded spheres, 250 parts of powdered alumina are mixed with 100 parts of purified silica sol containing 12% silica, 0.2 gram of magnesia added to the mixture and the mixture poured into moulds. At the end of a minute, hardening has taken place and the elements may be ejected from their moulds. After calcination, it is found that the porosity of the spheres has attained 42%.
- If on the contrary, maximum compactness is desired, care will be taken to increase the setting time, and during the setting period the mixture will be subjected to compacting by ram or by vibration. By way of example, the following is the method which may be adopted for making a compact refractory element of zirconium silicate.
- Five kilograms of a mixture of 65% natural zirconiferous sand and 35% zirconia flour is incorporated with 600 grams of purified silica sol containing 10% of silica and to the mixture is added 0.1 gram of magnesia acting as setting accelerator. The paste thus obtained is poured into a mould, for example a wooden mould, and the whole is subjected to vibration on a shaking table. Hardening takes place only after 30 minutes. The element is then taken from the mould and dried to remove the solvent.
- Another interesting use of silica sols according to the invention consists in the production of sealing or protective coatings on parts which have to be heated to a high temperature.
- The silica sol is applied either alone or in admixture with powdered materials, such

as metals or metallic oxides, which can be kept in suspension in the sol without producing the hardening thereof during use. This suspension may be sprayed or brushed on or fixed by impregnation in a vacuum.

It is possible also to use the silica sols described in this specification for binding the powders of metals or their derivatives such as oxides or silicates.

WHAT I CLAIM IS:—

1. A process for the preparation of a silica sol composed of colloidal silica, organic solvents, and water, comprising the successive steps of forming in known manner a silica organo-hydrosol composed of colloidal silica, one or more organic solvents, water and inorganic salts, adding to this organo-hydrosol an oxygen-containing solvent miscible or partially miscible with water, for example acetone, dioxan, methyl alcohol, ethyl alcohol, normal propyl alcohol, iso-propyl alcohol, tertiary butyl alcohol, or a mixture of such solvents, in sufficient quantity to produce the precipitation or flocculation of the inorganic salts it contains, and removing the precipitated or flocculated inorganic salts. 70
2. A process according to claim 1, in which ethyl silicate is added to the salt-free sol to increase the silica concentration of the purified sol and to simultaneously remove at least part of the residual water. 75
3. A process according to claim 1, in which silicon tetrachloride is added to the salt-free sol to increase the silica concentration of the purified sol and to simultaneously remove at least part of the residual water, the hydrochloric acid formed being subsequently removed either by blowing with dry air or by passage over an anion-exchange resin in hydroxyl form. 80
4. A process according to claim 1, in which to increase the silica concentration of the sol there is added to the salt-free sol with agitation a further organic solvent which is miscible with the oxygen-containing solvent already present in the sol and which does not serve as a dispersion medium for the colloidal silica, for example spirit of turpentine, trichlorethylene, diisobutylene, benzene or a mixture of these compounds, preferably in the proportion of 25% to 40% of the volume of the sol treated, whereafter the organic layer containing the concentrated silica sol is separated off. 85
5. A process according to claim 4 in which the concentration of the purified and concentrated silica sol is adjusted and the residual water is at least partly removed by the addition of ethyl silicate. 90
6. A process according to claim 4, in which the concentration of the purified and concentrated silica sol is adjusted and the residual water is at least partly removed by the addition of silicon tetrachloride, the 95
- 100
- 105
- 110
- 115
- 120
- 125

- hydrochloric acid formed being removed either by blowing with dry air or by the passage over an anion-exchange resin in hydroxy! form.

5 7. A process for the preparation of silica sol substantially as hereinbefore described in the Examples.

10 8. A silica sol prepared by a process according to any of claims 1 to 7.

15 9. A silica sol according to claim 8 composed of 8 to 35% by weight of silica, less than 5% water, less than 0.1% inorganic salts and 60—92% of the organic solvent miscible with water.

20 10. A refractory product comprising the solid product obtained by hardening a mixture of a silica sol according to claim 8 or 9, a setting accelerator, for example calcined magnesia, and a refractory material, for example silica, alumina, magnesia, zirconia, a carbide or a silicate, optionally subjecting the mixture during hardening to compacting by ramming or by vibration, and heating the said mixture after hardening, to an elevated temperature to remove the volatile part of the silica sol.

25 11. A refractory product comprising as a binder a silica sol prepared by a process according to claim 7.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1964.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.